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Description

This invention relates to diesel fuels, to additive packages for incorporation therein, and to their use.

Improved fuel economy is a constant objective of all users of internal combustion engines as the cost of the fuel is a major component of operating costs. This is especially true for users of internal combustion engines used to drive land vehicles, ships, or stationary engines. Even a small improvement in fuel economy can result in a valuable reduction of operating costs. In addition it is useful to reduce the emissions of internal combustion engines, and any improvement in fuel economy contributes to this objective. This is particularly true where the engine is fuelled with a heavy (i.e. relatively viscous and non-volatile) hydrocarbon fuel, as is the case with many marine diesel engines and other heavy diesel engines used to drive vehicles. Such fuels often contain relatively high contents of sulphur which, as is well known, is an important contributor to pollution caused by exhaust gases, and also have relatively poor combustion characteristics which can constitute a limiting factor in the performance of the diesel engine burning them.

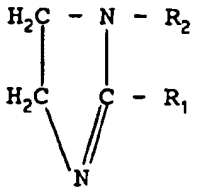
There is therefore a need to be able to improve combustion efficiency and economy of heavy diesel engines, especially marine diesel engines, which burn heavy hydrocarbon fuels especially those containing appreciable amounts of sulphur.

GB-A-1 413 323 discloses a nine component diesel fuel additive for reducing deposits formed by incomplete and inefficient combustion. The nine components include an amide derivative obtained by reaction of a polyolefin-substituted succinic acid or anhydride with a polyamine, and an organometallic tricarbonyl cyclopentadiene, together with other components said to be necessary to achieve the desired objective.

The present invention provides a heavy diesel fuel composition which has been shown to have improved combustion characteristics in use which lead to a valuable improvement in fuel economy and a reduction in the amount of exhaust gases produced. The heavy diesel fuel composition of the presentinvention comprises a cyclomatic manganese tricarbonyl (as hereinafter defined), an ashless dispersant comprising

(1) a product of a reaction between an ethylene polyamine mixture having an average of from 4 to 10 nitrogen atoms per molecule and a hydrocarbon-substituted carboxylic acid or anhydride made by reaction of a polyolefin having a molecular weight of from 500 to 5,000 with an unsaturated polycarboxylic acid or anhydride; or

(2) an imidazoline dispersant of formula



where R_1 represents a hydrocarbon group having 1 to 23 carbon atoms and R_2 represents a hydrogen atom or a hydrocarbon radical of 1 to 22 carbon atoms, or an aminoalkyl, acylaminoalkyl or hydroxyalkyl radical having 2 to 44 carbon atoms,

(3) an alkenyl succinic acid ester or diester made by reaction of polyolefin having a molecular weight from 500 to 5,000 with one or more alcohols containing 1-20 carbon atoms and 1-6 hydroxyl groups,

(4) an alkenyl succinic ester-amide made by reaction of polyolefin having a molecular weight from 500 to 5,000 with (a) one or more alcohols containing 1-20 carbon atoms and 1-6 hydroxyl groups, and (b) an amine,

(5) a Mannich condensates of hydrocarbyl-substituted phenols, formaldehyde or formaldehyde precursor, an amine having at least one primary amine group and containing 1-10 amine groups and 1-20 carbon atoms,

(6) a product of condensation of a cyclic anhydride with a straight chain N-alkylpolyamine of the formula $R\text{-}(NH\text{-}R'\text{-})_n\text{-}NH_2$, wherein n is an integer of 1 to 5, R is a linear hydrocarbon radical of 10 to 22 carbon atoms and R' is a divalent alkylene or alkylidene radical of 1 to 6 carbon atoms, or

(7) a product of reaction of an ethoxylated amine with a carboxylic acid of 8 to 30 carbon atoms,

and preferably also an antioxidant. The proportion of the cyclomatic manganese tricarbonyl compound should be from 0.00025 to 0.15%, preferably 0.000625 to 0.075% by weight based on the weight of the fuel. The proportion of the ashless dispersant should be from 0.0125 to 0.99%, preferably 0.025 to 0.495% by weight based on the weight of the fuel, and the proportion of the antioxidant (when present) should be from 0 to 0.2, usually

0.01 to 0.1% by weight based on the weight of the fuel.

The cyclomatic manganese tricarbonyl compound, the ashless dispersant and the optional antioxidant are conveniently supplied to the user, i.e. the supplier or user of the diesel fuel, in the form of a package comprising these ingredients, which may, if desired, be supplied in solution or stable dispersion in diesel fuel oil or other suitable diluent oil compatible with the diesel fuel into which the additives are to be incorporated, e.g. a mineral or synthetic lubricating oil, a hydrocarbon solvent, or an oxygenated hydrocarbon solvent such as an alcohol or ester. Such a package may contain from 1 to 15%, preferably 2.5 to 7.5% by weight of the cyclomatic manganese tricarbonyl compound, from 50 to 99%, preferably 70 to 90%, by weight of the ashless dispersant, and from 0 to 20% by weight of the optional antioxidant. The presence of the diluent oil is optional, but inclusion of such diluent can facilitate the incorporation of the package of additives into the diesel fuel. Typically, the package is incorporated in the fuel in a proportion of 0.025 to 1% by weight of the package based on the weight of the fuel, preferably 0.05 to 0.5% by weight.

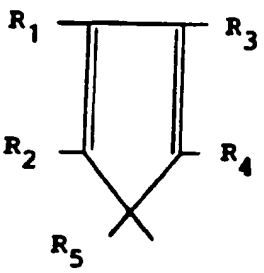
The present invention is especially useful for use with heavy diesel fuels for marine or railroad use. The requirements for such fuels have been laid down in numerous industrial standards. Reference may be made to ISO Standards DIS 8217 having the designations ISO-F- DMX, DMA, DMB, and DMC; to BSI Standards BS MA 100 (1982) classes M1, M2 and M3; and to the CIMAC 1 recommended standard. These are distillate marine fuel standards. Residual marine fuel standards have been issued by the same standardization authorities: ISO DIS DP 8217 having the designations ISO-F-RMA-10, RMB-10, RMC-10, RMD-15, RME-25, RMF-25, RMG-35, RMH-35, RMK-35, RML-35, RMH-45, RMK-45, RML-45, RMH-55 and RML-55; BSI Standards BSMA 100 (1982) classes M4, M5, M6, M7, M8, M9, M10, M11 and M12; and CIMAC recommended standards 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12. Such standards are described in, for example, ASTM Publication Code PCN 04-878000-12, "Marine Fuels" by Thornton et al December, 1983).

In general terms, the heavy diesel fuels in connection with which the present invention is especially useful contain at least 0.5% of sulphur, usually 1% or more up to about 5%. They have a density of at least 0.88 g/ml up to a maximum of about 1. The viscosity may vary from 10 to 500 centistokes (cSt) at 50°C, but is usually in the range of 100 to 500 cSt at 50°C.

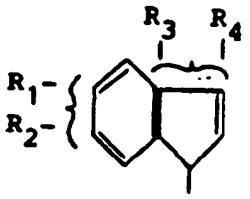
The cyclomatic manganese tricarbonyl compounds used in the present invention are described in the literature, for example US-A- 3015668. They may be represented by the general formula:

$$CyMn(CO)_3$$

where Cy represents a cyclomatic hydrocarbon radical, i.e. a hydrocarbon radical containing a cyclopentadienyl nucleus. Typical of such hydrocarbon radicals are those represented by the formulae:



and



where the radicals R_1, R_2, R_3, R_4 and R_5 are each hydrogen or a monovalent hydrocarbon radical, e.g. an alkyl radical of up to 4 carbon atoms, phenyl, or alkylphenyl in which the alkyl contains up to 4 carbon atoms. Preferred such radicals Cy contain from 5 to 13 carbon atoms each, and examples of the radical Cy are cyclopentadienyl, idenyl, methylcyclopentadienyl, propylcyclopentadienyl, diethylcyclopentadienyl, phenylcyclopentadienyl, tert-butyl-cyclopentadienyl, p-ethylphenylcyclopentadienyl and 4-tert-butyl indenyl. Specific preferred cyclomatic manganese tricarbonyl compounds which can be used in the present invention are cyclopentadienyl manganese tricarbonyl, methylcyclopentadienyl manganese tricarbonyl, indenyl manganese tricarbonyl, and ethylcyclopentadienyl manganese tricarbonyl. Methylcyclopentadienyl manganese tricarbonyl is commercially available and is preferred.

Ashless dispersants are described in numerous patent specifications, mainly as additives for use in lubricant compositions, but their use in hydrocarbon fuels has also been described. Ashless dispersants leave little or no metal containing residue on combustion. They generally contain only carbon, hydrogen, oxygen and nitrogen, but sometimes contain in addition other non-metallic elements such as phosphorus, sulphur or boron.

A preferred ashless dispersant is a product of a reaction between an alkylene polyamine and a hydrocar-

bon-substituted carboxylic acid or anhydride made by reaction of a polyolefin having a molecular weight from 500 to 5,000 with an unsaturated polycarboxylic acid or anhydride. These may be formed by conventional methods such as by heating the hydrocarbon substituted carboxylic acid or anhydride with the alkylene polyamine. The hydrocarbon-substituted anhydride may be made readily by heating a mixture of the olefin and maleic anhydride to 180°-220°C. The olefin is preferably a polymer or copolymer of a lower monoolefin such as ethylene, propylene, isobutene and the like. The more preferred source of alkenyl group is from polyisobutene having a molecular weight from 500 - 5,000. In a still more preferred embodiment the alkenyl is a polyisobutene group having a molecular weight of 700-5,000 and most preferably 900-2,000.

The preferred amines are the alkylene polyamines such as propylene diamine, dipropylene triamine, di-(1,2-butylene)triamine, tetra-(1,2-propylene)pentaamine.

The most preferred amines are the ethylene polyamines which have the formula $H_2N(CH_2CH_2NH)_nH$ wherein n is an integer from one to ten. These include: ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentaamine and pentaethylene hexamine, including mixtures thereof in which case n is the average value of the mixture. These ethylene polyamines have a primary amine group at each end so can form mono-alkenylsuccinimides and bisalkenyl-succinimides.

Thus especially preferred ashless dispersants for use in the present invention are the products of reaction of a polyethylenepolyamine, e.g. triethylene tetramine or tetraethylene pentamine, with a hydrocarbon substituted carboxylic acid or anhydride made by reaction of a polyolefin, preferably polyisobutene, having a molecular weight of 500 to 5,000, especially 900 to 1,200, with an unsaturated polycarboxylic acid or anhydride, e.g. maleic anhydride.

Another class of useful ashless dispersants includes alkenyl succinic acid esters and diesters of alcohols containing 1-20 carbon atoms and 1-6 hydroxyl groups. Representative examples are described in US 3,331,776; US 3,381,022 and US 3,522,179. The alkenyl succinic portion of these esters corresponds to the alkenyl succinic portion of the succinimides described above including the same preferred and most preferred sub-genus e.g. polyisobutenyl succinic acids wherein the polyisobutenyl group has an average molecular weight of 900-2,000.

Alcohols useful in preparing the esters include methanol, ethanol, isobutanol, octadecanol, eicosanol, ethylene glycol, diethylene glycol, tetraethylene glycol, diethylene glycol monethylether, propylene glycol, tripropylene glycol, glycerol, sorbitol, 1,1,1-trimethylol ethane, 1,1,1,-trimethylol propane, 1,1,1-trimethylol butane, pentaerythritol and dipentaerythritol.

The succinic esters are readily made by merely heating a mixture of alkenyl succinic acid, anhydrides or lower alkyl (e.g. C_1-C_4) ester with the alcohol while distilling out water or lower alkanol. In the case of acid-esters less alcohol is used. In fact, acid-esters made from alkenyl succinic anhydrides do not evolve water. In another method the alkenyl succinic acid or anhydride can be merely reacted with an appropriate alkylene oxide such as ethylene oxide and propylene oxide, including mixtures thereof.

In another embodiment the ashless dispersant is an alkenyl succinic ester-amide mixture. These may be made by heating the above-described alkenyl succinic acids, anhydrides or lower alkyl esters with an alcohol and an amine either sequentially or in a mixture. The alcohols and amines described above are also useful in this embodiment. Alternatively, amino alcohols can be used alone or with the alcohol and/or amine to form the ester-amide mixtures. The amino alcohol can contain 1-20 carbon atoms, 1-6 hydroxy groups and 1-4 amine nitrogen atoms. Examples are ethanolamine, diethanolamine, N-ethanol-diethylene triamine, trimethylol aminomethane.

Representative examples of suitable ester-amide mixtures are described in US 3,184,474; US 3,576,743; US 3,632,511; US 3,804,763; US 3,836,471; US 3,862,981; US 3,936,480; US 3,948,800; US 3,950,341; US 3,957,854; US 3,957,855; US 3,991,098; US 4,071,548 and US 4,173,540.

Such ashless dispersants containing alkenyl succinic residues may, and is well known, be post-reacted with boron compounds, phosphorus derivatives and/or carboxylic acid acylating agents, e.g. maleic anhydride.

Another useful class of ashless dispersants includes the Mannich condensates of hydrocarbyl-substituted phenols, formaldehyde or formaldehyde precursors (e.g. paraformaldehyde) and an amine having at least one primary amine group and containing 1-10 amine groups and 1-20 carbon atoms. Mannich condensates useful in this invention are described in US 3,442,808; US 3,448,047; US 3,539,633; US 3,591,598; US 3,600,372; US 3,634,515; US 3,697,574; US 3,703,536; US 3,704,308; US 3,725,480; US 3,726,882; US 3,736,357; US 3,751,365; US 3,756,953; US 3,793,202; US 3,798,165; US 3,798,247; US 3,803,039; and US 3,413,347.

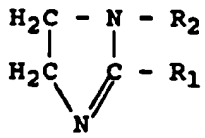
More preferred Mannich condensates are those made by condensing a polyisobutylphenol wherein the polyisobutyl group has an average molecular weight of 800-3,000 with formaldehyde or a formaldehyde precursor and an ethylene polyamine having the formula:

$$H_2N\{CH_2CH_2NH\}_nH$$

wherein n is an integer from one to ten or mixtures thereof especially those in which n has an average value

of 3-5.

Another class of ashless dispersants which can advantageously be used in the diesel fuel composition of the present invention are the imidazoline dispersants which can be represented by the formula:



wherein R_1 represents a hydrocarbon group having 1 to 23 carbon atoms, e.g. an alkyl or alkenyl group having 7 to 22 carbon atoms, and R_2 represents a hydrogen atom or a hydrocarbon radical of 1 to 22 carbon atoms, or an amino-alkyl, acylaminoalkyl or hydroxyalkyl radical having 2 to 44 carbon atoms. Such long-chain alkyl (or long-chain alkenyl) imidazoline compounds may be made by reaction of a corresponding long-chain fatty acid (of formula R_1-COOH), for example oleic acid, with an appropriate polyamine. The imidazoline formed is then ordinarily called, for example, oleylimidazoline where the radical R_1 represents the oleyl residue of oleic acid. Other suitable alkyl substituents in the 2- position of these imidazolines include undecyl, heptadecyl, lauryl and erucyl. Suitable N-substituents of the imidazolines (i.e. radicals R_2) include hydroxyalkyl, aminoalkyl, acylaminoalkyl and hydrocarbon radicals such as hydroxyethyl, aminoethyl, oleylaminoethyl and stearylaminoethyl.

Other suitable ashless dispersants which may be incorporated in the diesel fuel compositions of the present invention include the products of condensation of a cyclic anhydride with a straight-chain N-alkylpolyamine of the formula:

$$R\text{-}(NH\text{-}R'\text{-})_n\text{-}NH_2$$

where n is an integer at least equal to 1, usually 3 to 5, R is a saturated or unsaturated linear hydrocarbon radical of 10 to 22 carbon atoms and R' is a divalent alkylene or alkylidene radical of 1 to 6 carbon atoms. Examples of such polyamines include N-oleyl-1,3-propanediamine, N-stearyl-1,3-propanediamine, N-oleyl-1,3-butanediamine, N-oleyl-2-methyl-1,3-propanediamine, N-oleyl-1,3-pentanediamine, N-oleyl-2-ethyl-1,3-propanediamine, N-stearyl-1,3-butanediamine, N-stearyl-2-methyl-1,3-propanediamine, N-stearyl-1,3-pentanediamine, N-stearyl-2-ethyl-1,3-propanediamine, N-oleyl-dipropylenetriamine and N-stearyl-dipropylenetriamine. Such linear N-alkylpolyamines are condensed with, e.g., a succinic, maleic, phthalic or hexahydrophthalic acid anhydride which may be substituted by one or more radicals of up to 5 carbon atoms each.

Another class of ashless dispersant which can be incorporated in the compositions of the present invention are the products of reaction of an ethoxylated amine made by reaction of ammonia with ethylene oxide with a carboxylic acid of 8 to 30 carbon atoms. The ethoxylated amine may be, for example, mono-, di- or tri-ethanolamine or a polyethoxylated derivative thereof, and the carboxylic acid may be, for example, a straight or branched chain fatty acid of 10 to 22 carbon atoms, a naphthenic acid, a resinic acid or an alkyl aryl carboxylic acid.

All the aforesaid types of ashless dispersants are described in the literature and many are available commercially.

The heavy diesel fuel compositions of the present invention preferably include a combination of an ashless dispersant made by reaction of a polyolefin-succinic acid with a polyethylene polyamine and a long-chain alkyl imidazoline, preferably in a ratio of 1 to 4 to 4 to 1 by weight. Other mixtures of ashless dispersants can, of course, also be used.

The heavy diesel fuel compositions of the present invention preferably also contain an antioxidant, e.g. a phenolic, sulphurized phenolic, or aromatic amine antioxidant. Any commercially available antioxidant compatible with the diesel fuel may be used, but preferably the antioxidant is a hydrocarbon soluble phenolic antioxidant and especially such an antioxidant in which at least one ortho position of the phenol is blocked. Examples of such phenolic antioxidants are well known in the art. Examples include 2-tert-butylphenol, 2-ethyl-6-methylphenol, 2,6-di-tert-butyl-phenol, 2,6-di-tert-butyl-4-methylphenol, 2,2'-methylene-bis-4,6-di-tert-butylphenol, 4,4'-methylene-bis(2,6-di-tert-butyl-phenol) and 2,2'-propylidene-bis(6-tert-butyl-4-methyl-phenol). Mixtures of such antioxidants can also be used.

The heavy diesel fuel compositions of the present invention may also incorporate other additives commonly used in diesel fuels and compatible with the above-mentioned constituents. Such additional additives include: cold flow improvers and pour-point depressants, e.g. olefin/vinyl acetate copolymers such as ethylene/vinyl acetate copolymers and poly(alkylmethacrylates); corrosion inhibitors and antiwear additives based on carboxylic acids, such as dimerised linoleic acid, stabilisers, e.g. aliphatic amines such as dialkyl cyclohexylamine, and antifoam agents such as silicones. Such materials are well known in the art and are used in the usual pro-

portions.

The following Example illustrates the invention.

EXAMPLE

An additive mixture was prepared having the following composition:

Methylcyclopentadienyl manganese tricarbonyl;	4.7% by weight
Dispersant A;	52.6% " "
Dispersant B;	30.5% " "
2,6-di-tert-butyl-phenol	12.2% " "

Dispersant A was a polyisobutenyl succinimide ashless dispersant based on a polyisobutene having a number average molecular weight of 900 and triethylenetetramine. Dispersant B was a mixture of an imidazoline and an amide made by reaction of tall oil fatty acids with hydroxyethyl-ethylene diamine.

The mixture also included 100 solvent neutral mineral lubricating oil to facilitate incorporation into the heavy diesel fuel.

In the first experiment, residual marine diesel fuel having a viscosity of 115 cSt at 50°C and containing 1.9% of sulphur was treated with the aforesaid additive mixture at a treat rate of 0.066% by weight. When this treated diesel fuel was used in a single cylinder crosshead engine, a significant level of fuel economy was achieved, as compared with the untreated fuel or with the same fuel containing only the manganese compound at the same treatment rate.

In a second experiment, a residual marine diesel fuel having a viscosity of 465 cSt at 50°C and containing 3% sulphur was treated with the same additive mixture at the same rate. The fuel was used in an Atlas medium speed diesel engine having a maximum rpm of 1200. Tests were run across the full operating speed range of the engine under the conditions used during propulsion and with the power output of the engine controlled to the same level at each test speed both with the treated and the untreated fuel. Fuel consumption was determined by measuring the brake specific fuel consumption (BSFC) and the reduction in consumption obtained using the fuel containing the additive mixture compared with the consumption obtained with untreated fuel was determined. The results were as follows:

ENGINE SPEED RPM	% REDUCTION BSFC
Average over range 900-1200	1.4
1150	2.2

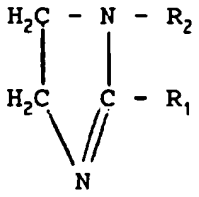
Having regard to the large amounts of fuel used by such engines, this represents a valuable increase in operating efficiency.

Further tests were carried out on a ship operating at sea and fitted with a Sulzer RD68 engine as the main propulsion engine and also with an auxiliary diesel engine for operating shipboard equipment. The main engine was fuelled with heavy residual marine diesel fuel having a viscosity of 100 cSt at 50°C and containing 4% sulphur. The auxiliary diesel engine was supplied with fuel having a viscosity of 15 cSt at 50°C and containing 2% sulphur. Each engine was supplied with untreated fuel for two weeks, then with treated fuel for two periods each of two weeks, and finally with untreated fuel again for a further period of two weeks. The treated fuel for the main engine contained 0.066% by weight of the additive package described above and the fuel for the auxiliary engine contained 0.05% by weight of the additive package described above.

It was found that the improvement in fuel economy (i.e. % reduction in fuel consumption) for the main engine was 1.5% and for the auxiliary engine was 2.5%.

Claims

1. A heavy diesel fuel composition comprising a heavy diesel fuel, a cyclomatic manganese tricarbonyl of general formula $CyMn(CO)_3$, wherein Cy is a hydrocarbon radical containing a cyclopentadienyl nucleus, and an ashless dispersant in which the ashless dispersant is
   (1) a product of a reaction between an ethylene polyamine mixture having an average of from 4 to 10 nitrogen atoms per molecule and a hydrocarbon-substituted carboxylic acid or anhydride made by reaction of a polyolefin having a molecular weight of from 500 to 5,000 with an unsaturated polycarboxylic acid or anhydride; or
   (2) an imidazoline dispersant of formula



   where R_1 represents a hydrocarbon group having 1 to 23 carbon atoms and R_2 represents a hydrogen atom or a hydrocarbon radical of 1 to 22 carbon atoms, or an aminoalkyl, acylaminoalkyl or hydroxyalkyl radical having 2 to 44 carbon atoms; or
   (3) an alkenyl succinic acid ester or diester made by reaction of polyolefin having a molecular weight from 500 to 5,000 with one or more alcohols containing 1-20 carbon atoms and 1-6 hydroxyl groups; or
   (4) an alkenyl succinic ester-amide made by reaction of polyolefin having a molecular weight from 500 to 5,000 with (a) one or more alcohols containing 1-20 carbon atoms and 1-6 hydroxyl groups, and (b) an amine; or
   (5) a Mannich condensate of hydrocarbyl-substituted phenols, formaldehyde or formaldehyde precursor, an amine having at least one primary amine group and containing 1-10 amine groups and 1-20 carbon atoms; or
   (6) a product of condensation of a cyclic anhydride with a straight chain N-alkylpolyamine of the formula $R\text{-}(NH\text{-}R'\text{-})_n\text{-}NH_2$, wherein n is an integer of 1 to 5, R is a linear hydrocarbon radical of 10 to 22 carbon atoms and R' is a divalent alkylene or alkylidene radical of 1 to 6 carbon atoms; or
   (7) a product of reaction of an ethoxylated amine with a carboxylic acid of 8 to 30 carbon atoms.

2. A composition according to claim 1 in which the proportion of the cyclomatic manganese tricarbonyl is from 0.00025 to 0.15% and the proportion of the ashless dispersant is from 0.0125 to 0.99%, both percentages being by weight based on the weight of the fuel.

3. A composition according to claim 1 in which the proportion of the cyclomatic manganese tricarbonyl is from 0.000625 to 0.075% by weight and the proportion of the ashless dispersant is from 0.025 to 0.495% by weight, both percentages being based on the weight of the fuel.

4. A composition according to any one of claims 1 to 3 in which the cyclomatic manganese tricarbonyl compound is cyclopentadienyl manganese tricarbonyl, methylcyclopentadienyl manganese tricarbonyl, indenyl manganese tricarbonyl, or ethylcyclopentadienyl manganese tricarbonyl.

5. A composition according to any of claims 1 to 4 in which the ashless dispersant comprises a mixture of (1) the product of reaction of triethylene tetramine or tetraethylene pentamine with the reaction product of a polyisobutene having a number average molecular weight in the range 900 to 1200 with maleic anhydride, and (2) an imidazoline dispersant of the formula specified in (2) of claim 1 wherein R_1 represents alkyl or alkenyl of 7 to 22 carbon atoms and R_2 represents hydroxyethyl.

6. A composition according to any one of claims 1 to 5 which also comprises an antioxidant.

7. A composition according to claim 6 in which the proportion of the antioxidant is 0.01 to 0.1% by weight based on the weight of the fuel.

8. A composition according to claim 6 or claim 7 in which the antioxidant is a hydrocarbon soluble phenolic antioxidant in which at least one ortho position of the phenol is blocked.

9. A composition according to claim 8 in which the phenolic antioxidant is 2,6-di-tert-butyl-phenol or 2,6-di-tert-butyl-4-methylphenol.

10. A composition according to any of claims 1 to 9 in which the heavy diesel fuel contains 1% or more of sulphur and has a viscosity in the range of 100 to 500 cSt ($mm^2 . s^{-1}$) at 50°C.

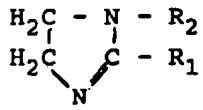
11. An additive package for incorporation in a heavy diesel fuel comprising a cyclomatic manganese tricarbonyl of general formula $CyMn(CO)_3$ as defined in claim 1 and an ashless dispersant according to (1) to (7) of claim 1.

12. A package according to claim 11 which also comprises an antioxidant and/or a diluent oil.

13. A package according to claim 12 which contains from 1 to 15% by weight of the cyclomatic manganese tricarbonyl compound, from 50 to 99% by weight of the ashless dispersant and from 0-20% by weight of the antioxidant.

Patentansprüche

1. Diesel-Kraftstoffzusammensetzung umfassend einen Diesel-Schwertreibstoff, ein cyclomatisches Mangantricarbonyl der allgemeinen Formel $CyMn(CO)_3$, in der Cy ein Kohlenwasserstoffrest mit einem Cyclopentadienylkern ist, und ein aschefreies Dispergiermittel, das
   (1) ein Reaktionsprodukt zwischen einer Ethylenpolyaminmischung mit durchschnittlich 4 bis 10 Stickstoffatomen pro Molekül und einer Kohlenwasserstoff-substituierten Carbonsäure oder einem -anhydrid, das durch die Umsetzung eines Polyolefins mit einem Molekulargewicht von 500 bis 5.000 mit einer ungesättigten Polycarbonsäure oder einem -anhydrid hergestellt wurde, oder
   (2) ein Imidazolin-Dispergiermittel der Formel



   in der R_1 eine Kohlenwasserstoffgruppe mit 1 bis 23 Kohlenstoffatomen und R_2 ein Wasserstoffatom, einen Kohlenwasserstoffrest mit 1 bis 22 Kohlenstoffatomen oder einen Aminoalkyl-, Acylaminoalkyl- oder Hydroxyalkylrest mit 2 bis 44 Kohlenstoffatomen bedeutet, oder
   (3) ein Alkenylbernsteinsäureester oder -diester, der durch die Umsetzung von Polyolefin mit einem Molekulargewicht von 500 bis 5.000 mit einem oder mehreren Alkoholen, die 1 - 20 Kohlenstoffatome oder 1 - 6 Hydroxylgruppen enthalten, hergestellt wurde, oder
   (4) ein Alkenylbernsteinsäureesteramid, das durch die Umsetzung von Polyolefin mit einem Molekulargewicht von 500 bis 5.000 mit (a) einem oder mehreren Alkoholen, die 1 - 20 Kohlenstoffatome und 1 - 6 Hydroxylgruppen enthalten, und (b) einem Amin hergestellt wurde, oder
   (5) ein Mannich-Kondensat aus Hydrocarbyl-substituierten Phenolen, Formaldehyd oder einer Formaldehydvorstufe, einem Amin, das mindestens eine primäre Amingruppe aufweist und 1 - 10 Amingruppen und 1 - 20 Kohlenstoffatome enthält, oder
   (6) ein Kondensationsprodukt aus einem cyclischen Anhydrid mit einem geradkettigen N-alkylpolyamin der Formel $R-(NH-R'-)_n-NH_2$, in der n eine ganze Zahl von 1 bis 5, R ein linearer Kohlenwasserstoffrest mit 10 bis 22 Kohlenstoffatomen und R' ein zweiwertiger Alkylen- oder Alkylidenrest mit 1 bis 6 Kohlenstoffatomen ist, oder
   (7) ein Produkt der Umsetzung eines ethoxylierten Amins mit einer Carbonsäure mit 8 bis 30 Kohlenstoffatomen
   ist.

2. Zusammensetzung nach Anspruch 1, in der der Anteil des cyclomatischen Mangantricarbonyls 0,00025 bis 0,15 % und der Anteil des aschefreien Dispergiermittels 0,0125 bis 0,99 % beträgt, wobei beide Ge-

wichtsprozentsätze auf das Gewicht des Treibstoffs bezogen sind.

3. Zusammensetzung nach Anspruch 1, in der der Anteil des cyclomatischen Mangantricarbonyls 0,000625 bis 0,075 Gew.% und der Anteil des aschefreien Dispergiermittels 0,025 bis 0,495 Gew.% beträgt, wobei beide Gewichtsprozentsätze auf das Gewicht des Treibstoffs bezogen sind.

4. Zusammensetzung nach einem der Ansprüche 1 bis 3, in der die cyclomatische Mangantricarbonylverbindung cyclopentadienylmangantricarbonyl, Methylcyclopentadienylmangantricarbonyl, Indenylmangantricarbonyl oder Ethylcyclopentadienylmangantricarbonyl ist.

5. Zusammensetzung nach einem der Ansprüche 1 bis 4, in der das aschefreie Dispergiermittel eine Mischung aus (1) dem Umsetzungprodukt von Triethylentetramin oder Tetraethylenpentamin mit dem Reaktionsprodukt eines Polyisobutens mit einem Zahlenmittel des Molekulargewichts im Bereich von 900 bis 1200 mit Maleinanhydrid und (2) einem Imidazoldispergiermittel der in (2) von Anspruch 1 angegebenen Formel, in der R_1 Alkyl oder Alkenyl mit 7 bis 22 Kohlenstoffatomen und R_2 Hydroxyethyl bedeutet, enthält.

6. Zusammensetzung nach einem der Ansprüche 1 bis 5, die außerdem ein Antioxidans enthält.

7. Zusammensetzung nach Anspruch 6, in der der Anteil des Antioxidans 0,01 bis 0,1 Gew.% bezogen auf das Gewicht des Treibstoffs beträgt.

8. Zusammensetzung nach Anspruch 6 oder 7, in der das Antioxidans ein in Kohlenwasserstoff lösliches phenolisches Antioxidans ist, in dem mindestens eine ortho-Stellung des Phenols blockiert ist.

9. Zusammensetzung nach Anspruch 8, in der das phenolische Antioxidans 2,6-Di-tert-butylphenol oder 2,6-Di-tert-butyl-4-methylphenol ist.

10. Zusammensetzung nach einem der Ansprüche 1 bis 9, in der der Diesel-Schwertreibstoff 1 % oder mehr Schwefel enthält und bei 50°C eine Viskosität im Bereich von 100 bis 500 cSt ($mm^2.s^{-1}$) aufweist.

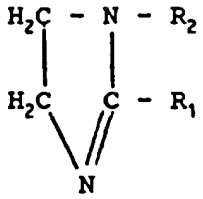
11. Additivpaket zur Inkorporierung in einen Diesel-Schwertreibstoff, das ein cyclomatisches Mangantricarbonyl der allgemeinen Formel $CyMn(CO)_3$ wie in Anspruch 1 definiert und ein aschefreies Dispergiermittel nach (1) bis (7) von Anspruch 1 enthält.

12. Paket nach Anspruch 11, das auch ein Antioxidans und/oder ein Verdünneröl enthält.

13. Paket nach Anspruch 12, das 1 bis 15 Gew.% cyclomatische Mangantricarbonylverbindung, 50 bis 99 Gew.% aschefreies Dispergiermittel und 0 bis 20 Gew.% Antioxidans enthält.

Revendications

1. Composition de combustible diesel lourd comprenant un combustible diesel lourd, un manganèse-tricarbonyle cyclomatique de formule générale $CyMn(CO_3)$, dans laquelle Cy représente un radical hydrocarboné contenant un noyau cyclopentadiényle, et un dispersant sans cendre, dans laquelle le dispersant sans cendre est
   (1) un produit d'une réaction entre un mélange d'éthylène-polyamines ayant un nombre moyen de 4 à 10 atomes d'azote par molécule et un acide ou anhydride carboxylique à substituant hydrocarboné préparé par réaction d'une polyoléfine ayant un poids moléculaire de 500 à 5000 avec un acide ou anhydride polycarboxylique insaturé ; ou
   (2) un dispersant à fonction imidazoline, de formule



dans laquelle R_1 représente un groupe hydrocarboné ayant 1 à 23 atomes de carbone et R_2 représente un atome d'hydrogène ou un radical hydrocarboné ayant 1 à 22 atomes de carbone, ou bien un radical aminoalkyle, acylaminoalkyle ou hydroxyalkyle ayant 2 à 44 atomes de carbone ; ou
(3) un ester ou diester d'acide alcénylsuccinique préparé par réaction d'une polyoléfine ayant un poids moléculaire de 500 à 5000 avec un ou plusieurs alcools contenant 1 à 20 atomes de carbone et 1 à 6 groupes hydroxyle ; ou
(4) un ester-amide alcénylsuccinique préparé par réaction d'une polyoléfine ayant un poids moléculaire de 500 à 5000 avec (a) un ou plusieurs alcools contenant 1 à 20 atomes de carbone et 1 à 6 groupes hydroxyle, et (b) une amine ; ou
(5) un produit de condensation de Mannich de phénols à substituant hydrocarbyle, de formaldéhyde ou d'un précurseur de formaldéhyde, d'une amine ayant au moins un groupe amine primaire et contenant 1 à 10 groupes amine et 1 à 20 atomes de carbone ; ou
(6) un produit de condensation d'un anhydride cyclique avec une N-alkylpolyamine à chaîne droite de formule $R\text{-}(NH\text{-}R'\text{-})_n\text{-}NH_2$, dans laquelle n est un nombre entier de 1 à 5, R représente un radical hydrocarboné linéaire ayant 10 à 22 atomes de carbone et R' représente un radical alkylène ou alkylidène divalent ayant 1 à 6 atomes de carbone ; ou
(7) un produit de réaction d'une amine éthoxylée avec un acide carboxylique ayant 8 à 30 atomes de carbone.

2. Composition suivant la revendication 1, dans laquelle la proportion du manganèse-tricarbonyle cyclomatique va de 0,00025 à 0,15 % et la proportion du dispersant sans cendre va de 0,0125 à 0,99 %, les pourcentages étant exprimés en poids sur la base du poids du combustible.

3. Composition suivant la revendication 1, dans laquelle la proportion du manganèse-tricarbonyle cyclomatique va de 0,000625 à 0,075 % en poids et la proportion du dispersant sans cendre va de 0,025 à 0,495 % en poids, les pourcentages étant basés sur le poids du combustible.

4. Composition suivant l'une quelconque des revendications 1 à 3, dans laquelle le manganèse-tricarbonyle cyclomatique est le cyclopentadiényl-manganèse tricarbonyle, le méthylcyclopentadiényl-manganèse-tricarbonyle, l'indényl-manganèse-tricarbonyle ou l'éthylcyclopentadiényl-manganèse-tricarbonyle.

5. Composition suivant l'une quelconque des revendications 1 à 4, dans laquelle le dispersant sans cendre comprend un mélange (1) du produit de réaction de la triéthylènetétramine ou de la tétraéthylènepentamine avec le produit de réaction d'un polyisobutène ayant une moyenne numérique du poids moléculaire de 900 à 1200 avec l'anhydride maléique, et (2) d'un dispersant à fonction imidazoline répondant à la formule spécifiée dans le paragraphe (2) de la revendication 1, dans laquelle R_1 représente un groupe alkyle ou alcényle ayant 7 à 22 atomes de carbone et R_2 représente un groupe hydroxyéthyle.

6. Composition suivant l'une quelconque des revendications 1 à 5, qui comprend également un anti-oxydant.

7. Composition suivant la revendication 6, dans laquelle la proportion de l'anti-oxydant va de 0,01 à 0,1 % en poids, sur la base du poids du combustible.

8. Composition suivant la revendication 6 ou la revendication 7, dans laquelle l'anti-oxydant est un antioxydant phénolique soluble dans les hydrocarbures, dans lequel au moins une position ortho du phénol est bloquée.

9. Composition suivant la revendication 8, dans laquelle l'anti-oxydant phénolique est le 2,6-di-tertio-butylphénol ou le 2,6-di-tertio-butyl-4-méthylphénol.

10. Composition suivant l'une quelconque des revendications 1 à 9, dans laquelle le combustible diesel lourd contient une quantité égale ou supérieure à 1 % de soufre et possède une viscosité de 100 à 500 cSt ($mm^2.s^{-1}$) à 50°C.

11. Multi-additif destiné à être incorporé à un combustible diesel lourd, comprenant un manganèse-tricarbonyle cyclomatique de formule générale $CyMn(CO)_3$ répondant à la définition suivant la revendication 1 et un dispersant sans cendre suivant les paragraphes (1) à (7) de la revendication 1.

12. Multi-additif suivant la revendication 11, qui comprend également un anti-oxydant et/ou une huile diluante.

13. Multi-additif suivant la revendication 12, qui contient 1 à 15 % en poids du manganèse-tricarbonyle cyclomatique, 50 à 99 % en poids du dispersant sans cendre et 0 à 20 % en poids de l'anti-oxydant.